

## METHANATION ACTIVITY OF SUPPORTED NICKEL ALLOYS

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### INTRODUCTION

Natural gas is a highly desirable fuel because of its high heating value and nonpolluting combustion products. In view of the expanding demand for and depletion of domestic supplies of clean fuels, economical production of synthetic natural gas (SNG) from coal ranks high on the list of national priorities.

Presently there are several gasification processes under development directed toward the production of methane or SNG. Although catalytic methanation of coal synthesis gas is an important cost item in the process, basic technological and design principles for this step are not well advanced. Extensive research and development are needed before the process can realize economical, reliable operation. Specifically, there appears to be important economic advantages in the development of more efficient, stable catalysts.

Extensive general reviews of pertinent literature dealing with methanation catalysts and kinetics have been provided by Greyson (1) and Mills and Steffgen (2). However, only recently, were kinetic studies of selected Group VIII metals (Fe, Ni, Co, Ru, Rh, Pt, Pd, Ir) reported by Vannice (3,4) and of nickel and ruthenium catalysts by Dalla Betta et al. (5,6) for which the kinetic data were clearly determined under conditions free of heat and mass transfer (diffusional) influences and for which specific rates were based upon active catalytic surface areas.

There is very little mention in previous literature in regard to alloy catalysts for methanation, and no previous kinetic data have been reported for alloy systems. This paper discusses recently determined methanation activity data determined for alumina-supported alloys of nickel with ruthenium, rhodium, molybdenum oxide, iron, cobalt, platinum, palladium and copper. These data were determined under conditions such that effects of heat and mass transfer were minimized and specific rates are reported at 1 atm and 225 and 250°C, based upon active catalytic surface areas.

### EXPERIMENTAL

#### Materials

Analytically pure metal salts (e.g. Baker Analyzed  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and Kaiser SAS 5x8 mesh alumina ( $301 \text{ m}^2/\text{g}$ ) were used in preparation of the supported nickel alloy catalysts. Samples were prepared by simple co-impregnation to incipient wetness of the support with aqueous metal salt solutions followed by oven drying at 80-100°C for 24 hours. The impregnated, dried samples were reduced in flowing hydrogen at 1000-2000 GHSV while heating at less than 5°C/min to 450-500°C with a one hour temperature hold at 230°C and 10-16 hours at 450-500°C. Samples reduced in a separate reduction system were carefully passivated with 1% air in nitrogen before transferring to the reactor.

Hydrogen and nitrogen gases (99.99%) were purified by simultaneously passing both through a palladium Deoxo purifier (Engelhard) and dehydrated molecular sieve or liquid nitrogen trap. Carbon monoxide (Matheson Purity; 99.99%) was used without further purification.

## Apparatus and Procedure

Metal surface areas were determined by means of hydrogen chemisorption at 25°C (Ni-Pd at 130°C) using a conventional volumetric apparatus capable of  $10^{-6}$  Torr. Hydrogen adsorption uptakes were determined as a function of pressure and the isotherm was extrapolated to obtain the adsorption at zero pressure. It was assumed that exactly one hydrogen atom adsorbed on each surface metal atom, and site densities were calculated based on the three lowest index planes of each metal (except in the case of Ni-MoO<sub>3</sub> where hydrogen was found to adsorb only on the nickel sites). The surface composition of each alloy was assumed to be the same as the nominal metal composition. Compositions and metal surface areas for catalysts prepared and tested in this study are listed in Table 1.

Methanation activities were measured using a laboratory, single-pass differential flow reactor equipped with Matheson flow meters and pressure regulators, a Hewlett-Packard 7132 temperature recorder, and a Hewlett-Packard 5830 gas chromatograph. A schematic of the reactor system is shown in Figure 1. The stainless steel reactor contained a catalyst chamber of 35cm<sup>3</sup> with adjustable thermocouples installed at each end of the chamber.

Differential activity measurements were carried out at low conversions with 2-4 grams of previously reduced (and passivated) catalyst in the reactor (the remainder of the bed was filled with pure Al<sub>2</sub>O<sub>3</sub> pellets) in order to minimize the influence of heat and mass transfer. The sample was heated in flowing H<sub>2</sub> (approximately 500 cm<sup>3</sup>/min) to 450°C and held for two hours at that temperature, then allowed to cool in flowing H<sub>2</sub> to about 225°C. Reactant gases (1% CO, 4% H<sub>2</sub> and 95% N<sub>2</sub>) were next allowed to flow through the reactor at a space velocity of 30,000 or 60,000 hr<sup>-1</sup> for 30 minutes during which time the reactor temperature was stabilized at 225, 250, or 275°C. Reactor pressure was usually about 5-8 psig. Three chromatographic samples of the product gas were obtained after which three additional chromatographic samples were taken to determine unconverted reactant gas concentrations. All important experimental conditions such as temperature and pressure were recorded at the time each chromatographic sample was taken.

## RESULTS AND DISCUSSION

Methanation activity data in the form of percent CO conversion, CH<sub>4</sub> production, and specific rates are listed for nickel and nickel alloy catalysts in Tables 2-4 (225°C, GHSV = 30,000 and 60,000 hr<sup>-1</sup> and 250°C, GHSV = 60,000 hr<sup>-1</sup>) and the specific rates are shown schematically in Figures 2 and 3 for 250°C and GHSV = 30,000 hr<sup>-1</sup>. For catalysts with low metal loadings, low conversions were obtained. For example, at 250°C (Table 4) conversions for the 3 wt.% catalysts (Ni-A-112, Ni-Ru, Ni-Rh, and Ni-MoO<sub>3</sub>) range from 4 to 14% depending upon the space velocity, whereas conversions for the 15 to 20 wt.% catalysts (all other catalysts) range from 11 to 43%. At 225°C the conversion ranges are 4 to 7% and 6 to 35% for low and high metal loadings respectively. Thus, truly differential (low conversion) conditions can be approached at 225°C for the 3% catalysts but not for the 15-20 wt.% catalysts. Apparently then, for our reactor system and for typical methanation catalysts, truly chemically-limited rate data can only be obtained for catalysts with a low metal loading (3-5 wt.%). Accordingly it would be desirable in obtaining very accurate kinetic rate data to prepare all of the catalysts with metal loadings in the 3-5% range. Nevertheless, for purposes of screening, the data obtained at moderate conversions are adequate for comparative purposes and satisfy the objectives of this study.

The turnover numbers ( $N_{CO}$  and  $N_{CH_4}$ ) shown in Tables 2-4 and Figure 3 indicate approximately the same order of magnitude activity for Ni, Ni-Ru, and Ni-Rh catalysts. Our turnover numbers agree well with the initial rates reported by Dalla Betta et al. (5) and Vannice (3) for 0.5% Ru/Al<sub>2</sub>O<sub>3</sub> and 5% Ni/Al<sub>2</sub>O<sub>3</sub>. It

appears that a small uncertainty (1-5%) in our results may be attributed to small variations in gas concentrations, pressure and flow rates over the test period of a given catalyst. The measurement of both activity and selectivity also includes uncertainties of 1-5% in calibration and measurement of gas concentrations. Thus, it may be possible that selectivities for  $\text{CH}_4$  are slightly higher than indicated, although there is undoubtedly significant hydrocarbon and  $\text{CO}_2$  production (3, 5).

Dalla Betta et al. (6) have indicated that their steady-state rates for methanation (after a 24-hour exposure to a reaction mixture) are 25 times lower than their initial rates (5). Thus, exposure to a reaction mixture over a period of hours or even minutes may significantly reduce the activity of the catalyst. This may explain why the turnover numbers reported in this study which were measured after exposure for 1/2 to 4 hours under reaction conditions are significantly lower than initial rates reported in the literature for 5%  $\text{Ni/ZrO}_2$  (5) and 5%  $\text{Ru/Al}_2\text{O}_3$  (3). The discrepancy between initial rates measured by Dalla Betta (5) and Vannice (3) for nickel and ruthenium catalysts might be similarly explained by differences in their pretreatment of the catalyst. Also, Vannice based his turnover numbers on  $\text{CO}$  adsorption data, which in fact may explain differences of 100-400% between his data and ours or those of Dalla Betta.

Vannice (3) has reported selectivities for the methanation reaction over the group VIII metals to be in the following decreasing order:  $\text{Pd} > \text{Pt} > \text{Ir} > \text{Ni} > \text{Rh} > \text{Co} > \text{Fe} > \text{Ru}$ . This order correlates well with measured selectivities for alloys of these same metals with nickel as shown in Tables 2-4. Of special interest is  $\text{Ni-Pt-A-100}$  which shows the highest selectivity, 99% at  $250^\circ\text{C}$  and higher temperatures. Changes in space velocity and temperature have appreciable effects on the selectivity as can be seen for example in the data for  $\text{Ni-A-112}$ ,  $\text{Ni-Pd-A-100}$  and  $\text{Ni-Ru-A-105}$ . Generally the selectivity increases with increasing temperature for a given space velocity and with increasing space velocity for a given temperature.

Figures 2 and 3 illustrate the magnitude of the rates per gram of catalyst, the turnover numbers, and selectivities at  $250^\circ\text{C}$  and a space velocity of  $30,000 \text{ hr}^{-1}$ . Nominal compositions and hydrogen uptakes used to calculate turnover numbers are listed in Table 1. It should be observed that the active metal loadings which vary significantly between catalysts have an obviously marked effect on the activity of the catalyst per unit catalyst weight as can be seen in Figure 2 where the listed order corresponds to the order of wt.% active metal. A comparison of these rates with the hydrogen uptake data shows that the rate is strongly influenced by the available surface area. For example,  $\text{Ni-A-116}$  (14 wt.% Nickel) is more active (per unit mass) than  $\text{G-87}$  (32 wt.% nickel) mainly because the surface area of the former catalyst is larger.

Turnover numbers for  $250^\circ\text{C}$  and a space velocity of  $30,000 \text{ hr}^{-1}$  are shown in decreasing order of activity in Figure 3.  $\text{Ni-MoO}_3\text{-A-101}$ ,  $\text{Ni-A-112}$  (3% nickel) and  $\text{Ni-Co-A-100}$  are the most active and  $\text{G-87}$  the least active. The details of these results are discussed below for each catalyst.

$\text{Ni-MoO}_3\text{-A-101}$  has a relatively low active surface area. Thus, its rate per unit weight is among the lowest tested. However, its turnover number is the highest of any catalyst tested. Assuming a method to increase the active surface area can be found, this catalyst is a most promising candidate for further study.

$\text{Ni-Ru-A-105}$  and  $\text{Ni-Rh-A-100}$  behave typically as nickel catalysts showing comparatively little effects of alloying although both are slightly less active than  $\text{Ni-A-112}$ , a nickel catalyst of comparable weight loading. The Rh does cause some increased selectivity to methane but not as pronounced as for platinum. The data determined at  $225^\circ\text{C}$  (Table 2) show an unexpectedly low selectivity to methane for  $\text{Ni-Rh}$ . Thus, some of this work will be repeated.

Ni-Co-A-100 contains a high loading of metal with equal weight percents of nickel and cobalt. It is of special interest in that both the rate per unit weight and the turnover number are high. The selectivity of this catalyst for the methanation reaction (78% at 250°C and GHSV = 30,000) is the lowest of any nickel catalyst tested. Vannice (3) has reported cobalt to have a selectivity of 78% under similar reaction conditions and the selectivity for nickel to be 90% also in good agreement with our data. Thus, cobalt has a strong effect on the selectivity of the Ni-Co catalyst. Nevertheless, a recent test showed the same catalyst to have a 93.5% selectivity at 225°C and GHSV = 30,000 hr<sup>-1</sup>. Since the selectivity should be lower at 225 than at 250°C, these data must be repeated.

Ni-Fe-A-100 was found to completely deactivate within two hours under normal reactor operating conditions. When the catalyst was removed from the reactor some of the beads showed a brown (rust) color as compared to the normal black. The observations suggest that the iron may scavenge the oxygen from the CO to form various iron oxides and thus effectively poison the catalyst. It is also possible that the Ni-Fe catalysts was not completely reduced at the beginning of the test. Additional reactor tests are planned to investigate these possibilities.

Ni-Pd-A-100 was found to be less active than most of alloys tested thus far with a turnover number about the same as G-87. Ni-Pt-A-100 has rate characteristics which are not outstandingly different from the other catalysts. The selectivity, however, is significantly improved over nickel. Vannice (3) has shown platinum to be one of the most selective catalysts for methane--namely about 98% to CH<sub>4</sub>. As an alloy with nickel in the amount of only one atomic percent platinum effects a 99% selectivity to methane.

Ni-A-116 is a high loading (15 wt.%) nickel catalyst used to compare against other catalysts containing 15-20 wt.% alloy. It has the highest rate per unit weight but has a turnover number the same as Ni-Pt-A-100 and somewhat lower than the cobalt alloy.

G-87 is a commercial nickel catalyst manufactured by Girdler Catalyst Corp. and is included as a comparison against other nickel catalysts. It is unique, however, from the other catalysts tested because it contains a different support of unknown composition which may influence the diffusional and mass transfer characteristics of the catalyst. Because of its high nickel loading (32 wt.%) it is expected that its rate per unit weight should be high. However, its turnover number is one of the lowest measured. This may be due in part to the effects of pore diffusion resistance at a relatively high conversion of CO.

Data on Ni-Cu-A-100 obtained at 250°C and a space velocity of 30,000 hr<sup>-1</sup> show this to be the least active catalyst tested thus far with relatively low selectivity. No further work is expected to be done with this catalyst because of its low activity.

Apparent activation energies for some of the nickel-alloy catalysts are listed in Table 5. With the exceptions of Ni-MoO<sub>3</sub>-A-101, Ni-Co-A-100, and Ni-Rh-A-100, the catalysts appear to have activation energies of 12-18 kcal/mole for both CO conversion and methane formation. Ni-Co-A-100 and Ni-Rh-A-100 have slightly higher values of 22.2 and 19.2 respectively. Ni-MoO<sub>3</sub>-A-101 has a significantly higher value of 26 kcal/mole which is close to the value of 25 kcal/mole for nickel reported by Vannice (3). The far right column lists the activation energies for various metals as reported by Vannice and measured under kinetic limited (low conversion) conditions. Considerably lower activation energies for alloys compared to those of either alloy component very likely result at least in part from mass transfer (or diffusional) limitations. In addition, the variations are partly the result of alloy formation, the alloy having catalytic properties different from either of the pure metals.

### CONCLUSIONS

1. Steady-state conversions of carbon monoxide at 225 and 250°C, 1 atm. (inlet composition of 1% CO, 4% H<sub>2</sub>, 95% N<sub>2</sub>) range from 3-43% for alumina-supported nickel alloy catalysts. Percent selectivities to methane range from 67-99%. Turnover numbers are not significantly different within experimental error for Ni-Rh, Ni-Ru, and Ni catalysts and compare favorably with initial rates reported for 5% Ni/Al<sub>2</sub>O<sub>3</sub> and 0.5% Ru/Al<sub>2</sub>O<sub>3</sub>.
2. Steady-state conversion measured at 225 and 250°C, 1 atm and for space velocities of 30,000 and 60,000 hr<sup>-1</sup> indicate that very nearly differential (low conversion) conditions obtain only for low (3-6 wt.%) metal loading catalysts. Screening data for 15-20 wt.% metal/Al<sub>2</sub>O<sub>3</sub> catalysts are influenced by mass transfer or diffusional limitations.
3. Ni-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> is the most active catalyst on a per surface area basis. Ni-Pt/Al<sub>2</sub>O<sub>3</sub> has the highest selectivity for methane production--namely 99% (250°C, 30,000 hr<sup>-1</sup>). A 14 wt.% Ni/Al<sub>2</sub>O<sub>3</sub> is the most active catalyst on a per mass basis--even more active than a commercial 32 wt.% Ni/Al<sub>2</sub>O<sub>3</sub> simply because the 14% catalyst has a high nickel surface area.

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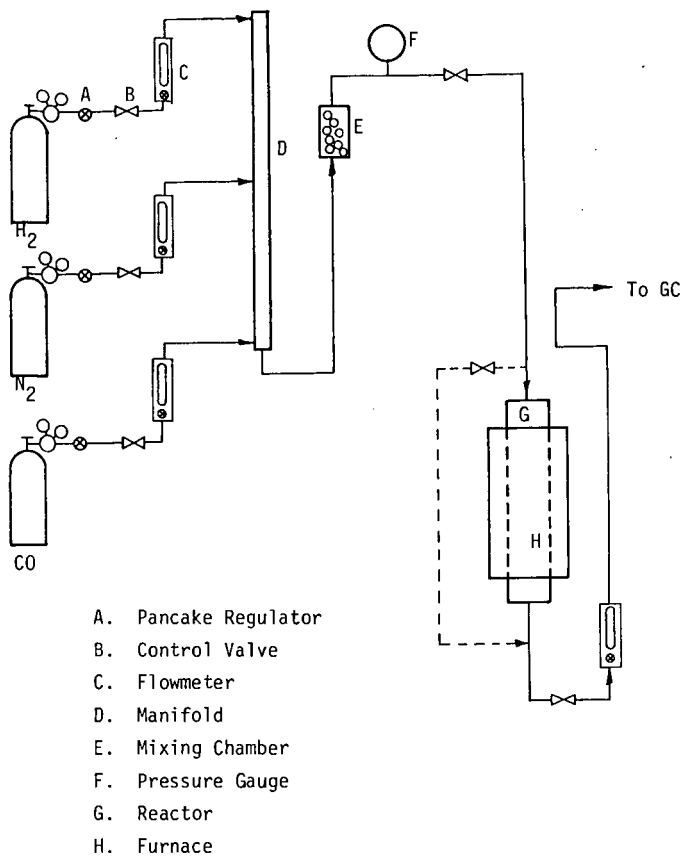


Figure 1 Low Pressure Continuous Flow Reactor System for Methanation Studies

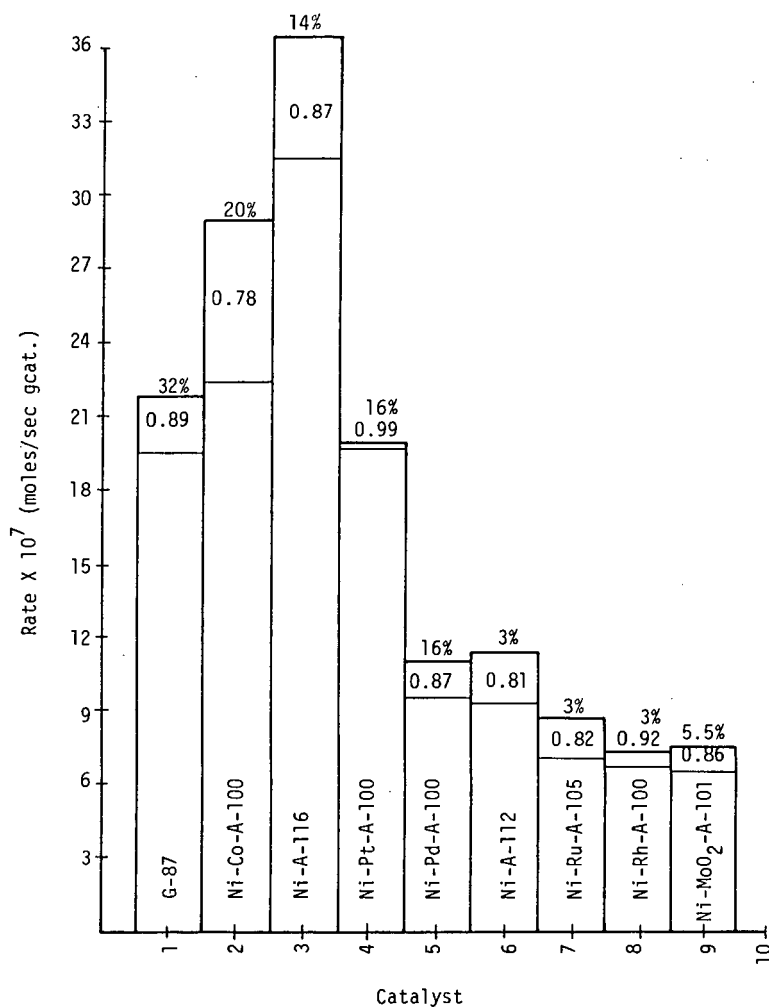


Figure 2 Specific Methanation Rates (mass basis) for Nickel and Nickel Alloy Catalysts. (Percentages are active metal loadings. Fractions represent selectivity to methane.) (T=250°C; GHSV=30,000 hr<sup>-1</sup>)

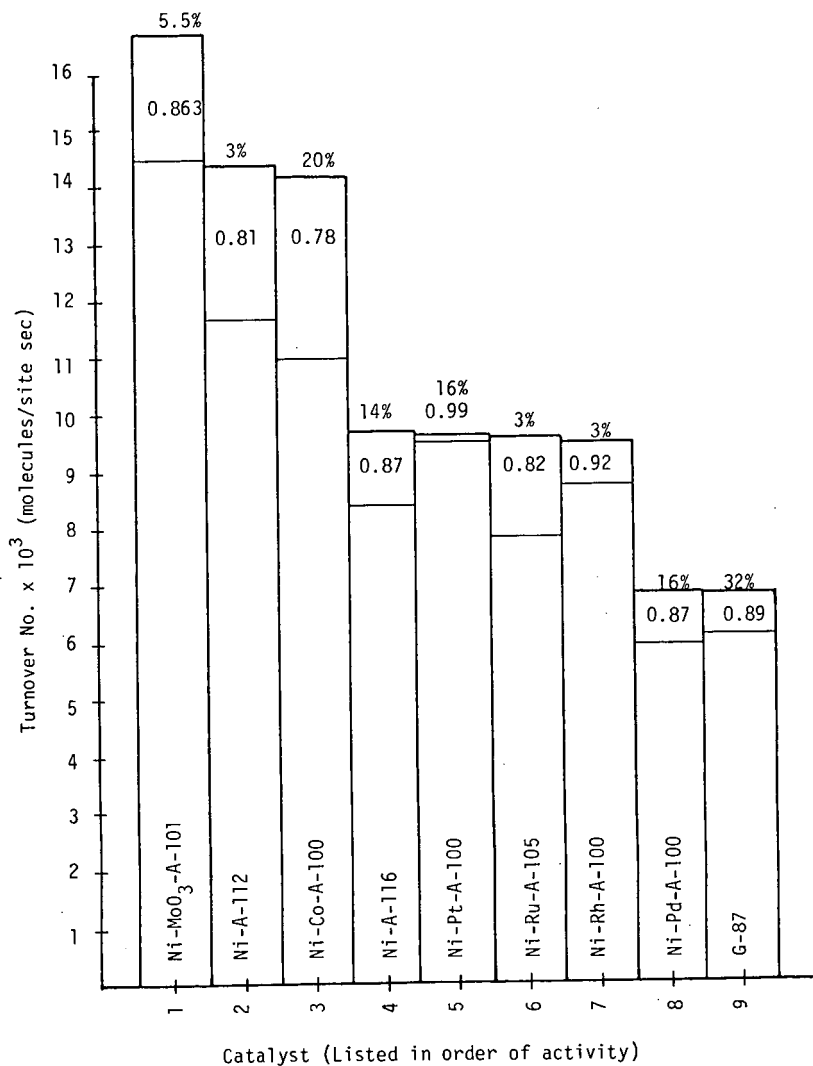


Figure 3 Turnover Numbers (molecules product/site sec) for Methanation on Nickel and Nickel Alloy Catalysts. (Percentages are active metal loadings. Fractions represent selectivity to methane.) (T=250°C; GHSV=30,000 hr<sup>-1</sup>)



TABLE 1

Hydrogen Chemisorptive Uptake Data for Alumina-Supported  
Nickel Nickel Alloy and Ruthenium Alloy Catalysts

Catalyst	Nominal Composition (wt%)	H <sub>2</sub> Uptake ( $\mu\text{moles/gram}$ )	Metal Particle Size ( $\text{\AA}$ )	Percent Dispersion	Surface Area ( $\text{m}^2/\text{g}$ )
Ni-A-111	3% Ni	21.4	116	8.35	1.75
Ni-A-112	3% Ni	39.4	63	15.4	3.23
Ni-A-116	14% Ni	187.8	62	15.7	15.39
G-87 (Girdler)	32% Ni	161.6	163	5.93	13.24
Ni-MoO <sub>3</sub> -A-101	2.5% Ni - 3% MoO <sub>3</sub>	22.5	92*	10.6*	1.84*
MoO <sub>3</sub> -A-101	3% MoO <sub>3</sub>	1.0	--	--	--
Ni-Ru-A-105	2.5% Ni - 0.5 wt% Ru	44.6	52	18.76	3.71
Ni-Rh-A-100	2.5% Ni - 0.5% Rh	38.3	62	16.1	3.16
Ni-Co-A-100	10% Ni - 10% Co	114.9	142	6.76	9.54
Ni-Fe-A-100	10% Ni - 10% Fe	80.6	278	4.60	5.14
Ni-Pt-A-100	15.7% Ni - 0.5% Pt	106	119	8.22	8.66
Ni-Pd-A-100	15% Ni - 1.0% Pd	107.4	115	8.13	8.82

\* Based upon nickel only

TABLE 2 Reactor Screening Data for Nickel and Nickel Alloy Catalysts  
225°C, GHSV = 30,000 hr<sup>-1</sup>, 16 psia

Catalyst	Conversion		Production		Rate x 10 <sup>7</sup> ( $\frac{\text{mole}}{\text{g sec}}$ )		Turnover # x 10 <sup>3</sup> (sec <sup>-1</sup> )		Selectivity to CH <sub>4</sub>
	$\frac{\text{CO}}{\text{CH}_4}$	$\frac{\text{CH}_4}{\text{CO}}$	$\frac{\text{CH}_4}{\text{Other}}$	$\frac{\text{Other}}{\text{CH}_4}$	$\frac{\text{CH}_4}{\text{CO}}$	$\frac{\text{CO}}{\text{CH}_4}$	$\frac{\text{CH}_4}{\text{CO}}$	$\frac{\text{CO}}{\text{CH}_4}$	
Ni-Co-A-100	16.2	15.15	1.05		9.31	9.96	4.56	4.88	0.935
Ni-Pt-A-100	16.77	15.20	1.60		9.91	10.95	4.77	5.27	0.906
Ni-Ru-A-105	5.18	3.48	1.73		2.79	4.17	3.12	4.68	0.672
Ni-Rh-A-100	3.3	2.2	1.1		1.48	2.21	1.93	2.88	0.671
Ni-Pd-A-100	6.9	6.67	0.2		4.62	4.79	2.87	2.97	0.97
Ni-MoO <sub>3</sub> -A-101	2.9	2.5	0.4		1.83	2.11	4.07	4.69	0.87
Ni-Fe-A-100	De-activates under reaction conditions								
G-87	22.45	19.55	2.88		9.81	11.25	3.04	3.49	0.871
Ni-A-112	6.63	4.47	2.13		3.62	5.35	4.60	6.80	0.674
Ni-A-116	34.63	28.08	6.55		19.23	23.74	5.13	6.32	0.815

TABLE 3 Reactor Screening Data for Nickel and Nickel Alloy Catalysts  
225°C, GHSV = 60,000 hr<sup>-1</sup>, 20 psia

Catalyst	% Conversion		% Production Other	Rate x 10 <sup>7</sup> (mole/g sec)		Turnover # x 10 <sup>3</sup> (sec <sup>-1</sup> )		Selectivity to CH <sub>4</sub>
	CO	CH <sub>4</sub>		CH <sub>4</sub>	CO	CH <sub>4</sub>	CO	
Ni-Co-A-100								
Ni-Pt-A-100	15.53	14.03	1.43	18.47	20.33	8.88	9.80	0.903
Ni-Ru-A-105	4.15	3.25	0.88	5.23	6.63	5.87	7.44	0.788
Ni-Rh-A-100								
Ni-Pd-A-100	6.63	5.43	1.23	7.76	9.49	4.81	5.89	0.817
Ni-MoO <sub>3</sub> -A-101	3.70	3.03	0.67	4.84	5.86	10.74	13.03	0.827
Ni-Fe-A-100								
De-activates under reaction conditions								
G-87	20.37	17.43	2.93	18.53	21.63	5.75	6.72	0.856
Ni-A-112	5.70	4.63	1.03	7.12	8.71	9.04	11.05	0.812
Ni-A-116	24.05	21.98	2.05	30.88	33.76	8.47	8.99	0.914

TABLE 4 Reactor Screening Data for Nickel and Nickel Alloy Catalysts  
250°C, GHSV = 60,000 hr<sup>-1</sup>, 20 psia

Catalyst	% Conversion		% Production Other	Rate x 10 <sup>7</sup> (mole/g sec)		Turnover # x 10 <sup>3</sup> (sec <sup>-1</sup> )		Selectivity to CH <sub>4</sub>
	CO	CH <sub>4</sub>		CH <sub>4</sub>	CO	CH <sub>4</sub>	CO	
Ni-Co-A-100	38.7	30.43	8.27	38.03	48.3	18.6	23.7	0.787
Ni-Pt-A-100								
Ni-Ru-A-105	9.47	8.03	1.47	12.70	14.97	14.20	16.80	0.848
Ni-Rh-A-100								
Ni-Pd-A-100	11.2	10.3	0.9	14.67	15.93	9.09	9.85	0.92
Ni-MoO <sub>3</sub> -A-101	9.3	8.7	0.65	13.56	14.58	30.14	32.41	0.92
Ni-Fe-A-100								
De-activates under reaction conditions								
G-87								
Ni-A-112	14.43	13.58	0.88	20.64	21.99	26.19	27.91	0.941
Ni-A-116	43.53	38.17	5.43	53.38	60.94	14.21	16.22	0.877

TABLE 5 Apparent Activation Energies for Methanation Catalysts  
Based on measurements at 225-250°C and a space velocity of 30,000 hr<sup>-1</sup>

Catalyst	CO Conversion (Kcal/mole)	CH <sub>4</sub> Production (Kcal/mole)	Metal*	CH <sub>4</sub> * Production Kcal/mole
Ni-Co-A-100	22.2	18.3	Co	27.0±4.4
Ni-Pt-A-100	12.4	14.3	Pt	16.3±0.8
Ni-Ru-A-105	14.8	19.0	Ru	24.2±1.2
Ni-Rh-A-100	19.2	21.1	Rh	24.0±0.4
Ni-Pd-A-100	17.1	14.8	Pd	19.7±1.6
Ni-MoO <sub>3</sub> -A-100	26.2	26.2		
Ni-Fe-A-100			Fe	21.3±0.9
G-87	13.7	14.2	Ni	25.0±1.2
Ni-A-112	15.5	19.2		
Ni-A-116	8.8	10.2		

\*Data of Al Vannice (Exxon) Ref.